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Molecular dynamics in hydrogen-bonded interactions: A preliminary experimentally determined harmonic stretching force field for HCN---HF

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Observation of the $2\nu_1$ overtone band in the hydrogen-bonded complex HCN---HF permits evaluation of the anharmonicity constant $X_{11} = -116.9(1)$ cm^{-1} and determination of the anharmonicity corrected fundamental frequency ω_1. This information, and available data from previous rovibrational analyses in the common and perdeuterated isotopic species of HCN---HF, offer an opportunity for calculation of an approximate stretching harmonic force field. With the assumptions $f_{12} = f_{24} = 0.0$, the remaining force constants (in mdyn/Å) are evaluated as: $f_{11} = 8.600(20)$, $f_{22} = 6.228(9)$, $f_{33} = 19.115(40)$, $f_{44} = 0.2413(39)$, $f_{13} = 0.000(13)$, $f_{14} = 0.0343(2)$, $f_{23} = -0.211(6)$, $f_{34} = 0.000(2)$. These compare to $f_{11} = 9.658(2)$ in the HF monomer and $f_{11} = 6.244(3)$ and $f_{33} = 18.707(16)$ in the HCN monomer. These results provide the information necessary to quantitatively assess the applicability of the Cummings and Wood approximation in this hydrogen-bonded complex and also give an estimate of D_j^e, the equilibrium distortion constant in the harmonic limit. Comparisons of these experimentally determined parameters with the predictions of *ab initio* molecular orbital calculations at several levels of approximation are presented.

INTRODUCTION

The determination of a quantitative anharmonic potential energy surface of hydrogen-bonded interactions is undoubtedly one of the most important aspects associated with the characterization of the fundamental nature of these species. However, to our knowledge no hydrogen-bonded species has had its anharmonic potential energy surface experimentally determined using spectroscopic methods. This current situation is not surprising, as anharmonic potential energy surfaces have only been determined for a small number of simple polyatomic molecules. These analyses are dependent on observation of a wide variety of fundamentals, overtones, hot bands, and combination bands, not only in the common species but also in a sufficient number of isotopically substituted species. This variety of bands is necessary to obtain a precise evaluation of their harmonic and anharmonic constants, along with anharmonic cross terms of the potential energy surface. In the case of small, stable polyatomic molecules (such as HCN and OCS),[1–3] the rovibrational analysis of a sufficient number of such vibrational bands has allowed a precise determination up to and including quartic terms of the potential energy surface. In hydrogen-bonded species such analyses are particularly difficult. The low concentration of such hydrogen-bonded dimers under static gas phase conditions appropriate for high resolution rovibrational analysis of vibrational bands is a severe problem. Indeed, it has only been recently that all the fundamentals bands of such a species have been rovibrationally analyzed.[4–8] Furthermore, the observation of a sufficient number of the even more weakly absorbing overtone bands, hot bands, and combination bands which permit such analyses has only been available in the last few months.[6,9,10] While supersonic jet and molecular beam spectroscopy hold optimism for greatly facilitating such analyses in the future, it will require substantial progress before such analyses can encompass the wide range of vibrational bands necessary for detailed quantitative characterization of such potential energy surfaces.

An approximate harmonic force field for the complex HCN---HF has been estimated previously.[11] However, this analysis was based on the results of low resolution infrared and approximate vibrational information based on the results of an extensive investigation by rotational microwave spectroscopy. This calculation did not include significant corrections for anharmonicity needed in the force field fit. The recent rovibrational analysis of the wide range of fundamentals, overtones, hot bands, and combination bands in both the common and perdeuterated isotopic species now permits an estimate of the anharmonically corrected fundamental frequencies for each stretching vibration in HCN---HF and DCN---DF. In particular, it is possible to attempt an approximate force field determination within the limitations of the previously described approximations.

As described, extensive information relevant to the characterization of the potential energy surface of HCN--HF (Tables I and II) has been obtained using medium resolution, static gas phase Fourier transform, and Doppler limited color center laser spectroscopy. While this information is not sufficient to evaluate an anharmonic potential energy surface for this species, there appears to be sufficient experimental information to estimate an appropriate anharmonic corrected stretching harmonic force field for this complex.

The fundamental frequencies ω_1, ω_2, ω_3, and ω_4 in HCN--HF are predictable with reliable estimates of their uncertainties. Although there is less experimental information available for corresponding analyses in DCN---DF, we

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are able to use certain approximations to estimate their respective values. There are thus eight fundamental harmonic frequencies available for generating the force field. A comprehensive analysis of the harmonic stretching force field requires availability of far more extensive information than that currently available. Such information would become available from similar rovibrational analyses of expensive complex isotopes involving $H^{13}C^{14}N$, $D^{13}C^{14}N$, $H^{12}C^{15}N$, and $D^{12}C^{15}N$, etc. Investigations of this kind would be expected to produce more reliable f_{ij} $(i \neq j)$ force constants, but would not be expected to significantly change the magnitude of primary f_{ii} force constants. The diagonal force constants obtained for HCN--HF are available for comparison with corresponding force constants determined in the two monomer components HF and HCN. This provides quantitative changes in these quadratic force constants on complex formation. Furthermore, such constants are also available for comparison with the increasing number of *ab initio* molecular orbital calculations for the HCN---HF complex.

In this paper, we report the observation of the overtone $2\nu_1$ in the complex HCN---HF, including the experimental evaluation of X_{11} in the complex. This data, together with other available information, enables determination of approximate anharmonically corrected frequencies for the four fundamental stretching vibrations in $^1H^{12}C^{14}N$---$^1H^{19}F$ and two vibrations in $^2H^{12}C^{14}N$---$^2H^{19}F$. The remaining two harmonic fundamental stretching frequencies of the deuterated species are estimated by several methods to establish a range of their respective values. The combination of these approximate harmonic fundamentals allow the determination of the harmonic force constants, f_{ij}. These force constants can in turn be used to test the validity of the Cummings and Wood[12] approximation for the first time. This approximation proposes a rather simple relation between the f_{ij}'s and the usual harmonic oscillator force constant. The Cummings and Wood approximation recognizes the separation of the motions of the relatively light mass of the hydrogen atom associated with the hydrogen bond and greatly simplifies the analysis of fundamental harmonic frequencies and frequency shifts due to deuteration.

Furthermore, it is now possible to compare the experimentally derived potential energy surface information to the wide range of *ab initio* molecular orbital calculations which have become available for the HCN---HF complex. In particular, the comparison of these experimental results with recent theoretical calculations by Bouteiller *et al.*,[13] the sophisicated CEPA (coupled electron pair approximation) stretching force field calculation of Botschwina,[14] and the simple and elegant electrostatic model of Liu *et al.*,[15] is possible. With Botschwina's calculations, a comparison can be made for the first time in both the harmonic and anharmonic approximation; thus, permitting a critical assessment of the current status of these calculations.

EXPERIMENTAL

In HCN---HF [a moderately strong hydrogen-bonded species in which the pressure broadening parameter is $\sim 27(6)$ MHz Torr^{-1}], it is desirable that the total pressure should be $\leqslant 5$ Torr to minimize the contribution of pressure broadening to the observed spectral linewidth of the complex and for reduction of spectral overlap due to intense monomer transitions. Under such conditions, the concentration of complex is typically in the range 10^{12}–10^{14} molecules/cc with corresponding ground state concentrations of 8×10^7–8×10^9 molecules cm^{-3}. Highly sensitive spectroscopic techniques capable of resolving the extensive band structure of hydrogen-bonded complexes are essential. To obtain the overtone spectrum of the HF stretching vibration in HCN---HF ($2\nu_1$) under the above restrictions a Bomen DA3-002 Fourier transform infrared spectrophotometer was used. This gas phase spectrum was recorded at 0.01 cm^{-1} resolution and required a total accumulated scan time of 8 h. The Fourier transform infrared spectrometer was used in conjunction with a temperature-controlled, corrosion resistant White cell and two calcium fluoride windows served as input and output couplers on the multipass cell. The transfer optics interfacing the interferometer and the White cell have been described previously.[16] The entire optics was evacuated to eliminate extraneous atmospheric absorptions. An absorption path length of 128 m was necessary in order to obtain the $2\nu_1$ vibrational spectrum, with a suitable signal-to-noise ratio ($\sim$20:1). An initial static gas mixture of 6 Torr HCN and 14 Torr HF was transferred into the multipass cell and subsequently cooled to 243.2 (0.5) K. As we were unable to rovibrationally resolve the final spectrum, it was observed at a total static gas pressure of 7.0 Torr. The small transition moment for the $2\nu_1$ transition ($\sim$0.034 D)[17] required that we use a detector which had a greater sensitivity than that of InSb at 7200 cm^{-1}. Thus, we employed a liquid nitrogen cooled Germanium detector which was approximately 30 times more sensitive than InSb in order to observe the $2\nu_1$ spectrum. The observed spectrum was characterized by pronounced P bandheads very similar to those observed in the ν_1 spectrum of HCN---HF.[6] We were unable to rovibrationally resolve the band presumably due to vibrational predissociation and high spectral density. However, a simulated band profile fit permitted us to estimate the band origin frequency at 7198.6(2) cm^{-1}. This assignment is further supported by the fact that the P bandheads from $2\nu_1$ $(\Sigma\rightarrow\Sigma)$ and $2\nu_1+\nu_7^1-\nu_7^1$ $(\Pi\rightarrow\Pi)$ were approximately separated by the anharmonic cross term $2X_{17}$. The anharmonicity constant X_{11} was determined to be $-116.9(1)$ cm^{-1} using the second order approximation of the energy expansion:

TABLE I. Experimental data for stretching force field of HCN--HF and DCN--DF.[a]

	Observed band origins (cm^{-1})			
	HCN--HF		DCN--DF	
i	ν_i	ω_i	ν_i	ω_i
1	3716.212(2)	3941.8(2)	2730.8909(2)	**
2	3310.3284(3)	3439.6(3)	2638.1309(1)	2711.8(2)
3	2120.935(1)	2153.4(2)	1943.0046(3)	1970.5(3)
4	168.33(2)	185.8(5)	···	**

[a] The ν_i are the observed band origins and the ω_i are the harmonic frequencies. The values in parentheses are the error associated with the given frequency. The ** are estimated and explained in the text.

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TABLE II. Anharmonicity and anharmonic cross terms (cm^{-1}).[a]

				HCN---HF			
X_{ij}	1	2	3	4	5	6	7
1	−116.9(1)	···	···	8.025(7)	···	···	4.216(5)
2		−51.26(1)	−14.61(22)	−0.161(1)	−18.98(2)	···	−0.409(2)
3			−10.45(38)	···	−3.61(22)	···	−0.61(2)
4				−2.01(1)	2.61(5)	−21.61(18)	1.00(5)

$|X_{12}|$, $|X_{13}|$, $|X_{15}|$, $|X_{26}|$ assumed $\leqslant 1\ cm^{-1}$
$|X_{34}|$, $|X_{36}|$ assumed $\leqslant 3\ cm^{-1}$
$|X_{16}|$, $\leqslant 10\ cm^{-1}$

				DCN---DF			
X_{ij}	1	2	3	4	5	6	7
1							
2		−20.50(36)	−32.40(26)	−0.641(3)	−15.80(24)	···	−0.60(2)
3			−6.84(28)	···	−3.01(20)	···	−0.62(3)
4							

[a] The anharmonic corrections are based on the vibrational term energy expression $G(v_1,\ldots, v_7) = \Sigma_i\omega_i(v_i + d_i/2) + \Sigma_i\Sigma_j\chi_{ij}(v_i + d_i/2)(v_j + d_j/2) + \Sigma_i\Sigma_j g_{ij}l_il_j$, where d_i is the degeneracy of ith mode and l_i is the angular quantum number associated with the bending vibrational mode.

$$X_{11} = [2\nu_1 - 2(\nu_1)]/2. \quad (1)$$

CALCULATIONS

The relevant spectroscopic data for HCN---HF and DCN---DF are presented in Tables I and II. Thus far the only missing fundamental frequency in Fig. 1 is ν_4 in DCN---DF, although this has been estimated to be 160.5 cm^{-1}.[18] The values of X_{ij} (where $i, j \geqslant i$) have been included as they are necessary constants for evaluation of the harmonic frequencies ω_i. The remaining part of the table is still under investigation and contains substantial information which will subsequently provide additional potential constants relevant to the complete characterization of the potential surface. Inspection of the available data in Table II supports the application of a Bradley–Urey force field approach, and leads us to suspect that of the missing X_{ij}'s, the only one of any significance is X_{16}.

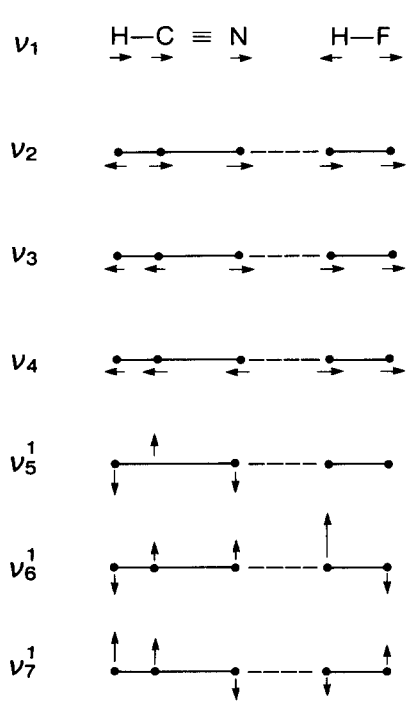

FIG. 1. The normal mode vibrations associated with the different frequencies.

The analysis of the anharmonic cross terms is based on the use of the familiar expression:

$$G(v_1,\ldots,v_7) = \Sigma_i\omega_i(v_i + d_i/2) + \Sigma_i\Sigma_j X_{ij}(v_i + d_i/2) \times (v_j + d_j/2) + \Sigma_i\Sigma_j g_{ij}l_il_j + \cdots, \quad (2)$$

where $G(v_1,\ldots,v_7)$ is the term energy dependent on the ith mode vibrational quantum number v_i, and l_i is the angular quantum number of the ith bending mode. The other constants are the harmonic frequency ω_i, the first order anharmonic coupling X_{ij}, and g_{ij}, the l_i dependence of degenerate vibrational states. The higher order terms of this expression were ignored in this analysis. Using this formulation of the term energy readily yields terms like X_{14} from combination bands such as $\nu_1 + \nu_4 - \nu_4$ when subtracted from ν_1. As revealed spectroscopically[5,7] and theoretically,[14] the shift in certain vibrational properties is expected to be small in the transition from HCN monomer to HCN in complexes. In particular, the ν_2 (H–C), ν_5 (HCN bend) and $\nu_2 - \nu_5$ interactions of the complex are expected to be almost identical to the corresponding monomer properties.[10,19] On that basis, some of the X_{ij} values of the monomer[1] are directly transferred into Table II. The data necessary for evaluation of all ω_i in HCN--HF, and ω_2 and ω_3 in DCN--DF is available.

The remaining harmonic stretching frequencies to be evaluated are the ω_1^D and ω_4^D of the DCN---DF complex. Certain of the necessary combination bands, hot bands, and overtone bands are not yet available for the deuterated com-

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plex. However, a range of values of ω_1^D are created to explore the sensitivity of the resultant force constants. One method of determining ω_1^D is to scale the anharmonic contribution to ν_1^D by the anharmonic contributions found in the associated monomer frequencies. The X_{11} corrections[32] for HF and DF monomers are -90.07 (X_{11}^H) and -45.71 (X_{11}^D) cm^{-1}, respectively. Multiplying the X_{11}^D/X_{11}^H ratio by the total anharmonic correction [which consists of the terms: $2X_{11} + \frac{1}{2}(X_{12}+X_{13}+X_{14}) + X_{15}+X_{16}+X_{17}$] for ν_1 of the HCN---HF complex yields a correction of -114.50 cm^{-1} to the ν_1^D (2730.89 cm^{-1}) value. The resulting value of ω_1^D (2845.39 cm^{-1}) is expected to be a lower bound to the harmonic frequency. The usual trend in anharmonic corrections of this type is for the X_{ii}^D term to be fairly represented by this ratioing technique, but the remaining X_{ij}^D ($i \neq j$) values of the complex do not decrease by nearly as much. This results in an underestimation of the overall anharmonic contribution and hence a low ω_1^D estimate. On the other hand, one can treat the HCN (or DCN) of the complex as a rigid body and evaluate the f_{11} and f_{44} values of the common species complex. These assumptions coupled with the invariant matrix properties of the value of the trace and determinant under a similarity transform result in the following equations:

$$\lambda_1 + \lambda_4 = f_{11}g_{11} + f_{44}g_{44}, \tag{3}$$

$$\lambda_1\lambda_4 = f_{11}f_{44}(g_{11}g_{44} - g_{14}^2), \tag{4}$$

where $\lambda_i = (2\pi c\omega_i)^2$. Solving these two equations for f_{11} and f_{44} gives the values 8.544 and 0.2413 mdyn/Å, respectively. With this estimate of f_{11}, the ω_1^D is 2860.32 cm^{-1}. Implicit in this calculation is the approximation that $f_{14} = 0$. This leads to an overestimate of f_{11} and thereby ω_1^D. These two estimates are used to bracket the actual value of ω_1^D. The best alternative seems to be the average of these two values or $\omega_1^D = 2852.8(70)$ cm^{-1}. This leaves the evaluation of ω_4^D. With all these values, the best approximation for this situation is the application of the Redlich–Teller equation[20] which reduces to the following simple form:

$$\frac{\omega_1^D\omega_2^D\omega_3^D\omega_4^D}{\omega_1\omega_2\omega_3\omega_4} = \left\{\left(\frac{m_H}{m_D}\right)^2\left(\frac{M_D}{M_H}\right)\right\}^{1/2}, \tag{5}$$

where m_D is the mass of deuterium and M_D is the total mass of the deuterated complex. With the averaged value of ω_1^D, the value of ω_4^D is 184.86 cm^{-1}. The estimated error in ω_1^D results in a very small uncertainty in determination of ω_4^D.

METHODOLOGY

Eight harmonic frequencies are thus available for determination of the harmonic force field. The standard *GF* matrix formulation[21] is used:

$$GFL = L\Lambda, \tag{6}$$

where the *G* matrix contains the reduced masses for the kinetic terms of the internal coordinates, the *F* matrix contains the force constants of the internal coordinate motions, the normal coordinate vectors are represented by *L*, and Λ contains the harmonic frequencies of the normal modes. Using the experimentally determined anharmonic contributions (i.e., X_{ij}), the observed frequencies (ν_i) are corrected to obtain the "observed" harmonic frequencies (ω_i^{ob}). The reduced masses are computed for the *G* matrix following conventional methods which require the isotopic masses and the equilibrium positions of the atoms in the complex. The force constants are estimated and the resultant coordinate vectors and normal mode frequencies (ω_i^c) are computed. The force constants are then varied by a Newton–Ralphson scheme to minimize the $\omega_i^{ob} - \omega_i^c$ differences. The weighting scheme of the calculation is proportional to the inverse square of the frequencies.

TABLE III. Harmonic force field fit for HCN---HF and DCN---DF.

f_{ij}	1	2	3	4
1	8.600(20)	a	0.000(3)	0.0343(2)
2		6.228(9)	−0.211(6)	a
3			19.115(40)	0.000(2)
4				0.2413(39)

HCN---HF		DCN---DF	
Calculated frequency	Error	Calculated frequency	Error
3940.8	1.0	2854.3	−1.4
3439.9	−0.3	2711.7	0.1
2153.9	−0.5	1968.9	1.6
186.6	−0.8	182.7	0.4

[a] These values of f_{ij} are forced equal to 0. The units of the force constants is mdyn/Å. The frequencies and errors are in units of cm^{-1}.

ANALYSIS

The results of the *GF* matrix calculation is presented in Table III. As can be seen by the table, the "long-range" couplings (f_{12} and f_{24}) are assumed to be zero. Also, the values of f_{22} and f_{23} are fixed to the monomer HCN[1] values. It is interesting to note that the f_{13} and f_{34} values are determined by the fit to be zero even though they are allowed to vary freely in the fit.

The normal coordinate analysis includes a potential energy distribution as well as the amplitudes of motion. The amplitudes of the common species for the C–H (ν_2) and C≡N (ν_3) modes are nearly pure; whereas, the C–D (ν_2) is in the approximate ratio of 2:1 (C–D to C≡N) and for the C≡N mode of the deuterated species the same ratio is 0.8:1. Similarly, the ν_2 and ν_3 modes in the potential energy distribution of HCN--HF are essentially pure. These same modes have force constant contributions of 2:1 for C–D to C≡N in ν_2 and 1:2 for C–D to C≡N in ν_3. These findings suggest considerable coupling for the deuterated species.

In regards to predissociative lifetimes in the two complexes,[18] the large coupling of ν_2 to ν_3 in the deuterated species (that is lacking in the common species) is suggestive. The density of states calculation indicates a lower density in the vicinity of ν_2 DCN--DF excited state relative to ν_2 of HCN--HF. However, the lifetime of the deuterated species is about three times shorter.[18] A viable explanation of the observed lifetime discrepancy is the faster vibrational relaxation through the ν_2 vibration of DCN--DF as a consequence

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of the large harmonic coupling of the ν_2 and ν_3 modes. In addition, the anharmonic cross terms X_{23} in HCN--HF and DCN--DF are -14.6 and -32.4 cm^{-1}, respectively. The larger anharmonic coupling in the deuterated complex also favors the argument of energy relaxation through vibrational coupling.

The diagonal quadratic force constants f_{11}, f_{22}, and f_{33} are of prime interest as they can be compared with the corresponding force constants in HF monomer (f_{11}) and HCN monomer (f_{22}, f_{33}). As expected, the f_{22} constant is slightly smaller but almost invariant under complex formation, reflecting the fact that this vibration does not participate to any great extent in such a weak complex formation. In contrast, the f_{11} constant 8.600(20) mdyn/Å is significantly less than the corresponding value of f_{11} in HF monomer. Indeed the force constant decreases by 1.5 mdyn/Å or 13% of its value in free HF and is associated with a shift in the very anharmonic well shape due to the electrostatic perturbation of complex formation.[15] The corresponding force constant f_{33}, 19.115(4) mdyn/Å increases by 0.408 mdyn/Å relative to the f_{33} in free HCN.

The corresponding value of f_{44} is of great topical interest[22] as it is the harmonic force constant associated with the ν_4 dissociative coordinate of the complex. This value is 0.2413(39) mdyn/Å. There have been many attempts to evaluate this parameter from D_j values in the microwave, microwave relative intensity measurements,[23] and from the band origin frequency of the ν_4 vibration. The latter[6] was determined to be 168.344 cm^{-1} which yields a f_{44} value of 0.193 mdyn/Å. However the anharmonic correction for determination of the ω_4 value to second order approximation is large, i.e.,

$$\omega_4 = \nu_4 - 2X_{44} - \tfrac{1}{2}(X_{14} + X_{24} + X_{34}) - (X_{45} + X_{46} + X_{47}),$$

primarily due to the large negative value of $X_{46} = -21.61(18)$ cm^{-1}. Also, there has been considerable interest in the literature regarding the magnitude of f_{14} the quadratic cross term involving the ν_s (in this case H–F) vibration in moderately strong hydrogen bonds and the dissociative coordinate ν_4. This term is clearly significant as far as prediction of vibrational predissociation from the ν_1 band of HCN---HF and will be discussed later.

COMPARISON TO APPROXIMATION SCHEMES

As mentioned in the description of setting the upper limit for the ω_1^{D} calculation, one of the approximations which appears to be effective is the neglect of the coupling (f_{14}) between the high and low frequency stretching modes. The resulting ω_1^{D} is somewhat but not excessively overestimated by this omission. In all the approximate ω_1^{D} calculations, it is assumed that the force field cross terms which couple the HF stretch or hydrogen bond stretch to the CN stretching mode (specifically, f_{13} and f_{34}) are zero. The force field calculation results are consistent with those assumptions [i.e., $f_{13} = 0.000(3)$ mdyn/Å and $f_{34} = 0.000(2)$ mdyn/Å]. If the lower limit (or upper limit) of ω_1^{D} is used, the primary effect is that the fit to the ω_1 and ω_4 for the two isotopic species is worsened. However, f_{11}, f_{14}, and f_{44} only change by 1% to 2%, justifying this particular assumption. Obviously, more information on the deuterated species along with other isotopically labeled complexes such as $^1H^{13}C^{14}N$--$^1H^{19}F$ would improve the standard deviation of the fit of f_{14} but sufficient information is at hand to warrant this initial approximate evaluation. An interesting aspect of the current force field calculation is the essentially zero values of the fitted coupling terms f_{13} and f_{34}. The long-range 1–3 interaction is not surprisingly small. However, the vanishing of the 3–4 interaction suggests a bottleneck in vibrational energy transfer processes that warrants further investigation and has particular significance with respect to observed predissociative lifetimes in the ν_3 states of HCN--HF and DCN--DF. Once these force field values are obtained, the calculation of other potential surface parameters through the use of approximation schemes can be exploited to test approximations used in the literature.

One particularly useful approximation scheme for hydrogen-bonded interactions is that of Cummings and Wood.[12] This approximation scheme manifests itself through the following statements: (1) the low frequency hydrogen bond stretch and high frequency HF stretch are independent of the other vibrational modes, (2) the kinetic energy matrix elements $g_{11} \approx g_{44} \approx g_{14} \approx 1/m_{\mathrm{H}}$ (i.e., the proton mass in these expressions is much smaller than the other contributing masses), and (3) HCN is a rigid body. With these assumptions, the resulting GF formulation allows the collection of f_{ij} terms to calculate an effective force constant (f_i^{eff}) for the two stretching modes. These relationships are

$$f_1^{\mathrm{eff}} = (f_{11} - 2f_{14} - f_{44}), \tag{7}$$

$$f_4^{\mathrm{eff}} = (f_{44}f_{11} - f_{14}^2)/(f_{11} - 2f_{14} + f_{44}). \tag{8}$$

These effective force constants are in fact the normal mode force constants which are related to the harmonic frequencies ω_1 and ω_4 through the equation

$$\omega_i = \frac{1}{2\pi c}\left(\frac{f^{\mathrm{eff}}}{\mu_i}\right)^{1/2}. \tag{9}$$

The resulting values based on our force field constants are: (1) $\omega_1^{\mathrm{H}} = 3944.3$ cm^{-1} and $\omega_1^{\mathrm{D}} = 2859.4$ cm^{-1} (compared to the experimental values of $\omega_1^{\mathrm{H}} = 3941.8$ cm^{-1} and $\omega_1^{\mathrm{D}} = 2852.9$ cm^{-1}) and (2) $\omega_4^{\mathrm{H}} = 186.8$ cm^{-1} and $\omega_4^{\mathrm{D}} = 182.8$ cm^{-1} (compared to $\omega_4^{\mathrm{H}} = 185.8$ cm^{-1} and $\omega_4^{\mathrm{D}} = 184.9$ cm^{-1}). This method of estimation of the harmonic frequencies for this hydrogen-bonded complex appears to be quite good.

It is interesting to note that the difference between the Cummings and Wood approximation and the earlier, upper limit approximation of ω_1^{D} arises in two different aspects of the GF matrix formulation. The Cummings and Wood approximation reduces the kinematic portion of the calculation to a proton moving against infinite masses (i.e., $g_{11} \approx g_{44} \approx g_{14} \approx 1/m_{\mathrm{H}}$). The upper limit approximation of ω_1^{D} ignores the potential energy coupling between the high and low frequency modes ω_1 and ω_4 (i.e., $f_{14} \approx 0$). In all other respects, these two approaches are the same and they both produce comparable results [i.e., ω_1^{D} (Cummings and Wood) $= 2859.4$ cm^{-1} and ω_1^{D} (upper limit) $= 2860.3$

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cm^{-1}]. This lends additional support to the notion that the actual ω_1^D value is probably closer to the upper limit value than the lower limit value.

The current investigation of the harmonic stretching force field for the HCN--HF complex allows the testing of several other approximate calculations[25,26] intended to predict the important hydrogen-bond stretching force constants k_σ (k_4 in HCN--HF) and their corresponding vibrational frequencies. The availability of precisely determined ground state rotational (B_0) and distortion (D_J^0) constants from microwave spectroscopy[23] has lead to numerous predictions of such force constants, particularly within the pseudodiatomic approximation and in a more sophisticated approach[24] which inertial properties are explicitly considered. In the pseudodiatomic approximation[25]

$$D_J = 4B_D^3/\omega^2 \text{ and } k_4 = 4\pi^2\mu\omega_4^2c^2 \tag{10}$$

(where the subscript D indicates the dimer value of a particular constant) which give values of $k_4 = 0.1975$ mdyn/Å and $\omega_4 = 170.8$ cm^{-1} which is compared with the values of $k_4 = 0.2413$ mdyn/Å and $\omega_4 = 185.8$ cm^{-1} determined in this work. In the more sophisticated approach,[24] k_4 is expressed as

$$k_4 = 16\pi^2\mu_D c^2 B_D^3/D_J(1 - B_D/B_{HF} - B_D/B_{HCN}). \tag{11}$$

This equation yields $k_4 = 0.2311$ mdyn/Å which is only 4% low relative to the experimentally determined value. In both approximation schemes [Eqs. (10) and (11)], the ground state rotational and distortion constants were used.

Another approximation that can be tested is the evaluation of the equilibrium distortion constant D_J^e. The D_J^e is computed using the assumption that only the significant contribution is found in the weak bond force field constant (in our case f_{44}). For a linear dimer, D_J^e (in units of s^{-1}) is given by

$$hD_J^e = h^4/8I^4\Sigma_i\Sigma_j J_{xx}^{(i)}(f^{-1})_{ij}J_{xx}^{(i)} \tag{12}$$

in which I is the principle moment of inertia, $J_{xx}^{(i)} = \delta I_{xx}/\delta R_i$ where R_i is the ith internal coordinate, and $(f^{-1})_{ij}$ is the i,jth matrix element of the inverse F matrix (referred to as a compliance constant). In this approximation all compliance constants are set to zero except for the one which refers to the weak bond stretch. Calculation of the compliance matrix clearly shows that this is a reasonable assumption. All values of the compliance matrix are two orders of magnitude smaller than f_{44}^{-1} with the exception of f_{11}^{-1} which is nearly 40 times smaller. Using our experimentally determined f_{ij}^{-1}'s and J_{ij}'s, the value of D_J^e is found to be 5.787 kHz. By comparison, the diatomic approximation [Eq. (10)] for the evaluation of D_J^e yields a value of 6.401 kHz. These two values fall within the error bounds of the experimentally determined D_J^e value of 5.90(50) kHz.

The calculation of B_e and D_J^e and their subsequent use in Eqs. (10) and (11) now needs to be addressed. Our recent rovibrational analyses permit the estimation of B_e and D_J^e using the expressions

$$B_v = B_e - \Sigma_i\alpha_i(v_i + d_i/2) + \Sigma_i\gamma_{ii}l_i^2, \tag{13}$$

$$D_v = D_J^e + \Sigma_i\beta_i(v_i + d_i/2), \tag{14}$$

B_e and D_J^e are 3675.4(10) MHz and 5.90(50) kHz, respectively. This contrasts the values of $B_0 = 3591.155$ MHz, as determined from microwave data[23] and 3591.187 MHz, as determined from combined microwave/infrared fits[28] along with corresponding D_J^0 values of 6.99 and 7.07 kHz. Use of the equilibrium molecular constants in evaluation of k_4 from Eq. (11) gives a value of 0.2296 mdyn/Å and a corresponding $\omega_4 = 178.8$ cm^{-1}. These are in good agreement with force field evaluation of 0.2413 mdyn/Å and 185.8 cm^{-1}. Substitution of B_e and D_J^e into Eq. (10) (the pseudodiatomic case) predicts the corresponding ω_4 and k_4 values to be 193.5 cm^{-1} and 0.2535 mdyn/Å, respectively. In the pseudodiatomic case the values are significantly overestimated and explain the fortuitous agreement with our infrared analysis when ground state constants are used in this calculation.

COMPARISON TO *AB INITIO* CALCULATIONS

In addition to the approximate potential surface constant computations, there are *ab initio* calculations[13–15,29,30] of the harmonic frequencies (ω_i) and anharmonic frequencies (ν_i) that merit some comparative analysis with these experimentally determined ω_i's and ν_i's. Table IV displays the relevant comparisons of the experimental harmonic frequencies ω_i, vs different computational schemes. Included with the frequencies are the frequency shifts from the corresponding monomer units that comprise the complex (HF and HCN, or DF and DCN). They are enclosed in parentheses next to the ω_i. As one proceeds across Table IV, the basis sets and computational schemes become more sophisticated. The general trend is to overestimate the harmonic frequency of the stretching vibrations with the exception of the hydrogen bond stretch ω_4. A large contribution to the calculation of the ω_4 frequency is the X_{46} term, which indicates a strong coupling of the low frequency intermolecular hydrogen bond stretch to the high frequency intermolecular hydrogen bond bending vibration. In all calculations cited, this coupling is ignored, contributing to the underestimation of the ω_4 *ab initio* value. As far as an overall prediction based on the coupled four-dimensional potential surface describing the stretching modes is concerned, the CEPA-1 calculation fared best in terms of absolute values of ω_i's and in ω_i shifts from the monomer subunits. Unfortunately, the CEPA-1 calculations have not yet been extended to the case of DCN---DF. However, the completeness of the calculations for HCN---HF allowed a comparison of the computed anharmonic contribution to the harmonic frequencies ($\omega_i - \nu_i$) which could be compared to our estimated experimental values. In all cases but the highest frequency (HF), the theoretical values are an underestimation. It is anticipated that of all the X_{ij} values that we could not obtain, the X_{16} is most likely the remaining hold out of any significant size; although, its magnitude is expected to be such that $|X_{16}| \leqslant 10$ cm^{-1}. Using a value of $X_{16} = -10$ cm^{-1} in our calculation, leaves the SCF and CEPA-1 values for $\omega_i - \nu_1$ still slightly too large (Table V). The overall trend is still consistent with Botschwina's contention that the CEPA-1 potential is a bet-

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TABLE IV. *Ab initio* calculations of harmonic frequencies and shifts of frequencies from corresponding monomer units of HCN---HF and DCN---DF.

	HCN---HF							
	Experimental	(4-31G)[a]	10s–6p[b]	10s–6p[b]	DZ + P[c]	TZ + ZP[c]	SCF[d]	CEPA-1[d]
ω_1	3941.8[f]	3990	3945	3990	4332	4300	4294	3992
	(−196)[g]	(−127)			(−189)	(−171)	(−164)	(−168)
ω_2	3439.6[e]	3682			3638	3593	3602	3439
	(−1.6)	(−13)			(0)	(−7)	(−2)	(−3)
ω_3	2153.4[e]	2396			2437	2427	2428	2182
	(+24.7)	(+12)			(+31)	(+19)	(+21)	(+28)
ω_4	185.8	193.2	183.5	178.4	176	159	154	173

	DCN---DF					
	Experimental	(4-31G)[a]	10s–6p[b]	10s–6p[1 b]	DZ + P[c]	TZ + ZP[c]
ω_1	2852.9[f]	2891	2863	2891	3134	3118
	(−145.4)	(−93)			(−162)	(−123)
ω_2	2711.8[e]	2950			2933	2910
	(+8.5)	(+2)			(+14)	(+7)
ω_3	1970.5[e]	2157			2178	2159
	(+18.4)	(+4)			(+17)	(+8)
ω_4	184.9	189.0	182.5	177.7	172	155

[a] The results of Curtiss and Pople (Ref. 29) calculations using a 4-31G basis set.
[b] The results of Bouteiller, Allavena, and Leclercq (Ref. 13). The prime represents a counterpoise corrected function, for the Dunning basis set.
[c] The results of Somasundram, Amas, and Handy (Ref. 30).
[d] Work of Botschwina (Ref. 14) using a 110 CGTO basis set for both calculations.
[e] Based on the work of Nakagawa and Morino (Ref. 1).
[f] Values from Herzberg (Ref. 32).
[g] The values in parentheses represent the shift of the corresponding calculated monomer frequency. All values are in cm^{-1}.

ter computational tool than the ""straight" SCF type of calculation for this hydrogen-bonded system. It is pertinent to note that the CEPA-1 calculation was carried out for vibrations of A symmetry only. The potential surface associated with E vibration was not explored. When anharmonicity of the stretching coordinate only are applied to our observed stretching frequencies ν_i, the correlation with CEPA-1 values is excellent. When however, anharmonic cross term corrections X_{st} (s—stretch and t—bend) are incorporated in these calculations there are significant deviations from our experimental results. This indicates that the experimentally determined $X_{ss'}$ contributions agree with the CEPA-1 evaluation of these contributions. This contention is reinforced by the comparison of potential surface parameters and vibrational frequencies obtained using the same basis set (110 contracted Gaussian-type orbitals, CGTO's) in an SCF calculation and one incorporating the CEPA-1 potential. One final interesting comparison between these two calculations is the calculation of X_{22} and X_{33} of the HCN monomer which undergo very small changes in the complex. Once again the CEPA-1 generated values of $X_{22} = -52.9$ cm^{-1} and $X_{33} = 9.25$ cm^{-1}, which compare more favorably with the experimental values of -51.3 and -10.45 cm^{-1} as opposed to the SCF values of $X_{22} = -44.4$ cm^{-1} and $X_{33} = -9.25$ cm^{-1}.

Another interesting and novel approach to the hydrogen-bond theoretical picture has been recently developed by Dykstra *et al.*[15,31] His rather extensive treatment of the dipole–dipole, dipole–quadrupole, dipole–octopole, quadrupole–octopole interactions of pure electrostatic and induced polarization effects presents arguments as to the dominating effects characterizing the nature of this hydrogen bond. In this respect, two models: (1) valence bond considerations and (2) pure electrostatic interactions—have been used to

TABLE V. *Ab initio* calculations of anharmonic frequencies, shifts of frequencies, and anharmonic corrections for HCN---HF.

	Experimental		SCF[a]		CEPA-1[a]	
i	ν_i	$\omega_i - \nu_i$	ν_i	$\omega_i - \nu_i$	ν_i	$\omega_i - \nu_i$
1	3716.21(−245.2)[b]	226	4053(−242)	241	3738(−245)	254
2	3310.33(−1.14)	129	3505(0)	97	3326(+1)	113
3	2120.94(+24.08)	32	2405(+19)	23	2155(+27)	27
4	168.33	18	147	7	169	4

[a] Calculations by Botschwina (Ref. 14) using a 10 CGTO basis set for both calculations.
[b] The values in parentheses are the frequency shifts from the corresponding monomer units of the complex. All values are in cm^{-1}.

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account for different experimentally determined features of hydrogen-bonded complexes.[34,35] If one models the hydrogen-bonded complex as two monomer units perturbed by a linear multipole interaction potential, many properties of HF with HF, N_2, CO, HCCH, and HCN have been properly taken into account.[31] In terms of the long-range multipole interactions, both electrostatic and induced polarization effects contribute in these systems although the electrostatic contribution is larger. Among the changes that a linear interaction potential can produce are the very large frequency shifts found in HF. Because the HF stretching mode is so highly anharmonic, a linear interaction potential causes perturbations in the vibrational energy level structure that can not occur in a harmonic oscillator. Based on this long-range interaction potential in HCN---HF, Liu and Dykstra calculate that the total electrostatic contribution to the HF vibrational level spacing shift for the fundamental ($\Delta E_{0\text{-}1}$) to be 116 cm^{-1}. The experimental shift, $\Delta E_{0\text{-}1}$, for HCN---HF is found to be 251 cm^{-1}. Two primary approximations are involved in this approach: (1) a neglect of torsional vibrational coupling and other couplings which would tend to increase the vibrational shift and (2) the "strong" interaction of HCN---HF which makes the electrostatic model less appropriate. Putting those limitations aside, Liu and Dykstra[15] make predictions of the first overtone ($\Delta E_{0\text{-}2}$) and first hot band ($\Delta E_{1\text{-}2}$) shifts. Their prediction of $\Delta E_{0\text{-}2} = 509\ cm^{-1}$ compares favorably with our experimental determination of 552(1) cm^{-1} [i.e., $2\nu_{HF} = 7750.8(2)\ cm^{-1}$; $2\nu_1^{HCN\text{---}HF} = 7198.6(5)\ cm^{-1}$]. Using the same electrostatic model, Benzel and Dykstra[31] use a pseudodiatomic vibrational analysis of HCN---HF and estimate $\omega_4 = 197\ cm^{-1}$. Although this value is too high, it may prove interesting to investigate if the electrostatic model may produce upper bounds of this vibrational motion and the usual SCF calculations may set a lower bound of this type of frequency evaluation.

CONCLUSIONS

In HCN---HF, 22 anharmonicity constants and anharmonic cross terms X_{ij} are required to characterize the stretching frequency expansion within the second order approximation. We have been able to determine 15 of these constants. The magnitudes of four of the remaining constants are expected to be $\leqslant 1\ cm^{-1}$; thus, having negligible influence on the determination of the force field. Of the remaining undetermined constants, $|X_{34}|$ and $|X_{36}|$ are expected to be $\leqslant 3\ cm^{-1}$ while the X_{16} constant is more problematic. Although it is desirable to evaluate X_{16}, we have been unable to detect the combination band $\nu_1 + \nu_6$ using techniques which are currently available to us. Clearly a significantly more sensitive spectrometer will be necessary to detect the $\nu_1 + \nu_6$ band. However, the magnitude of X_{16} is expected to be less than or equal to 10 cm^{-1} and would be expected to contribute a maximum of 0.2% error to the determination of ω_1 of HCN---HF; therefore, its influence on the determined harmonic force constants should be minimal. Within these minor limitations, we have been able to determine an approximate harmonic stretching force field based on anharmonicity corrected vibrational frequencies in HCN---HF and DCN---DF. The determined force constants provide a set of parameters which give quantitative information sensitive to changes of bonding upon complex formation. In particular their values can be correlated to predictions based on currently available *ab initio* molecular orbital calculations. Furthermore, the analysis gives information on the relative contributions of the force constants, particularly the off-diagonal coupling constants. Extension of rovibrational band analyses to other isotopic species of HCN---HF can be expected to improve determination of the force field. However, these investigations should not significantly change the diagonal force constants although they may have some influence on the off-diagonal coupling constants. Apart from the f_{23} coupling term (which is assumed to be the same as in HCN monomer) only the f_{14} coupling constant has a significant value. Indeed, this value is $\sim 12\%$ of the f_{44} force constant. This determination of f_{14} provides a molecular parameter which is of significance in modeling vibrational predissociation from the ν_1 metastable states of HCN---HF and DCN---DF. In particular, it includes information which is relevant to theoretical modeling of the channels of energy transfer and reaction dynamics associated vibrational predissociation.[33] Furthermore, it is a parameter which has been incorporated in numerous theories proposed to explain line broadening mechanisms in hydrogen-bond H–X stretching vibrations. The f_{44} constant is determined to be 0.2422 mdyn/Å a value which is influenced by the large X_{46} correction to the fundamental frequency ν_4.

From the resulting stretching force field, we are able to test quantitatively the applicability of the Cummings and Wood approximation to the specific case of the hydrogen bond HCN---HF. The proposed model assumes (i) that normal mode ν_1 is effectively a mode in which the hydrogen atom vibrates against the heavy atom and (ii) a normal mode ν_4 in which the heavy atoms move along the molecular symmetry axis while the hydrogen atom continually readjusts its position to achieve the equilibrium HF bond length appropriate to the instantaneous N–F distance. The current analysis is in excellent quantitative agreement with the proposed model.

A complete force field analysis of a hydrogen-bonded complex would provide a bench mark for other experimental and theoretical work. In particular, a complete characterization of such a system allows a theoretical dissection of major contributions to absolute frequencies, frequency shifts, and potential surface parameters. With the addition of more isotopically labeled complexes and the inclusion of certain frequencies in both the common and perdeuterated species a more certain assessment of the harmonic and anharmonic contributions to the observed frequencies of the HCN---HF complex will be possible. As discussed earlier, better estimates of vibrational frequencies would be accomplished through a selective incorporation of stretch–bend coupling, especially for large-amplitude motions found in weakly bound complexes. For the HCN---HF system the rather large (in magnitude) X_{46} cross term suggests this particular combination to be important. Likewise, some preliminary investigations have suggested that the cubic coupling term k_{466} to be rather large in magnitude, further supporting the

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notion that this particular stretch–bend combination is important in *ab initio* calculations of vibrational potential surfaces.

Above all, the current analysis has provided a set of quadratic force constants in HCN---HF suitable for comparison with the monomer components HCN and HF. Furthermore, such constants are available for comparison with corresponding values in similar simple systems, while at the same time contributing to a data base of force constants which will find application in modeling of the force fields in more complex hydrogen-bonded systems.

Note Added in Proof: Previous calculations and conclusions in this paper are based on neglect of Fermi resonance interactions. Recent millimeter and far infrared spectra of HCN---HF demonstrate that such an interaction exists between the $\nu_4(\Sigma)$ and $2\nu_7^0(\Sigma)$ states of the complex. Current analysis only permits us to estimate a maximum Fermi resonance interaction energy of 13.2 cm^{-1} between these states. Force field calculations based on this correction result in lower limits of $f_{44} = 0.2056(30)$ and $f_{14} = 0.0297(20)$ mdyn/Å; other force constants, however, are not significantly affected. The best average values that we can propose for f_{44} and f_{14} at this time are 0.224(18) and 0.032(2) mdyn/Å, respectively. The corresponding value of B_ϵ is 3681.1(10) MHz.

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